#19 UB 8/16/01

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of Takuo HIBI et al.

Serial No. : 09/249,100 Group Art Unit : 1754

Filed : February 12,1999 Examiner : N. M. Nguyen

For : PROCESS FOR PRODUCING CHLORINE

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DECLARATION UNDER 37 C.F.R. §1.132

Honorable Commissioner of Patents and Trademarks

Washington, D.C. 20231

Sir:

I, Kohei SEKI, a Japanese citizen residing at 2-14-13-402, Imai, Chuo-ku, Chiba-shi, Chiba, Japan,
declare:

That I graduated from Hokkaido University, Faculty of Science in March 1995, and graduated Graduate School of Environmental Earth Science, Hokkaido University in March 1997, and entered Sumitomo Chemical Company Limited in April 1997, in which company I have since then been engaged in study of development of catalysts, especially the catalysts for oxidation of hydrogen chloride;

That I am familiar with the prosecution history of the above-identified application;

That I am one of the inventors of the identified-application;

That the following experiment was conducted by me or under my direct supervision.

EXPERIMENT

Experimental 1

A supported catalyst in which RuO_2 was supported on rutile TiO_2 carrier was prepared in the same manner as in Example 4 in the specification of the above-identified application.

Electron microscope analysis of the catalyst was conducted under the following conditions.

Instrument: FE-TEM HF-2000(manufactured by HITACHI Limited) (Transmittance type electron microscope)

Measuring condition: Acceleration voltage; 200kV,

Multiplication of photograph: ×1,500,000

As a result, as shown in **Photo. 1**, coagulated particles of RuO_2 were not observed., and this result was different from that obtained by using anatase TiO2 as described below.

Experimental 2

A supported catalyst in which RuO_2 was supported on anatase TiO_2 carrier was prepared in the same manner as in Example 3 in the specification of the above-identified application.

Electron microscope analysis of the catalyst was conducted under the same conditions as those of Experimental 1.

As a result, as shown in Photo. 2, RuO_2 was observed as many particles. Arrows in **Photo. 2** indicate the particles.

Experimental 3

A catalyst was prepared by the following process. That is, 50.0 g of a titanium oxide powder (P25, 17% rutile crystal, manufactured by Nippon AEROSIL Co., Ltd.) was kneaded with 31.0 g of pure water and 13.2 g of a titanium oxide sol (CSB, TiO_2

content: 38% by weight, manufactured by Sakai Chemical Industry Co., Ltd.). At room temperature, a dry air was blown to the kneaded one, which was then dried until suitable viscosity was obtained. After drying, the mixture was sufficiently kneaded again. The kneaded one was extruded into a form of a noodle of 1.5 mmϕ in size. After drying under air at 60℃ for 4 hours, 33.4 g of a white noodle-shaped titanium oxide was obtained. 15.2g of a noodle was sampled from 33.4 g of a noodle. And after heating under air from room temperature to 500℃ over 1.3 hours, calcination was conducted at the same temperature for 3 hours. After the completion of the calcination, 15.0 g of a white extruded titanium oxide carrier was obtained by cutting the noodle-shaped solid into pieces of about 5 mm in size. Then, 5.0 g of this carrier was impregnated with an aqueous solution prepared by dissolving 0.20 g of commercially available ruthenium chloride ($RuCl_3.nH_2O$, Ru content: 37.3% by weight) in 1.7 g of pure water, and dried at 60℃ for 2 hours. Then, the resulting solid was dipped in a solution of 1.05 g of a 2N potassium hydroxide solution and 1.5 g of pure water. Next, to the potassium hydroxide solution, a solution of 0.255 g of hydrazine monohydrate and 2.5 g of pure water was added under nitrogen at room temperature. Bubbling occurred on dipping. After 60 minutes, filtration was conducted by using a glass filter. Washing was conducted for 30 minutes by adding 500 ml of water, followed by filtration. This operation was repeated five times. The pH of the wash was 8.8 at the first time, and the pH of the wash was 7.5 at the fifth time. To the extruded solid separated by filtration, 25 g of a 2 N of potassium chloride solution was added and, after stirring, the extruded solid was separated by filtration again. This operation was repeated three times. The resulting solid was dried at 60℃ for 4 hours to obtain a gray solid. After heating from room temperature to 350℃ in an air over 1 hour, the solid was

calcined at the same temperature for 3 hours. After the completion of the calcination, 500 ml of pure water was added and the mixture was stirred and, furthermore, the solid was separated by filtration. This operation was repeated five times and, after adding dropwise an aqueous silver nitrate solution to the wash, it was confirmed that potassium chloride is not remained. Then, 4.7 g of a bluish gray extruded ruthenium oxide catalyst supported on titanium oxide was obtained by drying this solid at 60℃ for 4 hours.

Incidentally, the calculated value of the content of ruthenium oxide was as follows.

$RuO_2/(RuO_2 + TiO_2) \times 100 = 1.95\%$ by weight

The calculated value of the content of ruthenium was as follows.

$Ru/(RuO_2 + TiO_2) \times 100 = 1.5\%$ by weight

X-ray diffraction analysis of the titanium oxide powder (P25) used was conducted under the following conditions.

Apparatus: Rotaflex RU200B (manufactured by Rigaku Co.)

X-ray type: Cu $K\alpha$

X-ray output: 40 kV-40 mA

Divergence slit: 1°

Scattering slit: 1°

Receiving slit: 0.15 mm

Scanning speed: 1° /min.

Scanning speed: $5.0\text{-}75.0^\circ$

Monochromator: curved crystal monochromator is used

The proportion of a peak intensity (381cps) of a rutile crystal ($2\theta=27.4^\circ$) to a total value of a peak intensity (381 cps) of a rutile crystal () and a peak intensity (1914 cps) of an anatase crystal ($2\theta=25.3^\circ$) was 17%. Consequently, the content of the rutile crystal was 17%.

Electron microscope analysis of the catalyst was conducted under the same conditions as those of Experimental 1.

As a result, as shown in **Photo. 3**, RuO_2 was observed as many particles.

The above results are collected and shown in Table 1.

Table 1

Experimental	Crystal structure of TiO_2	Particles of the RuO_2 in TEM photo.
1	Rutile	Not observed
2	Anatase	Observed
3	Rutile/anatase 17/83	Observed

<u>CONSIDERATION</u>

From the comparison of Experimental 1 with Experimental 2 and Experimental 3, it became clear that the structure of RuO_2 in the catalyst prepared by using rutile TiO_2 is wholly different from that in the catalyst prepared by using anatase TiO_2 or 17wt%rutile/83%anatase TiO_2.

That I declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the above identified application or patent issued thereon.

Signed this 3rd day of August, 2001.

Kohei Seki

Kohei SEKI

Photo. 1

Photo. 2

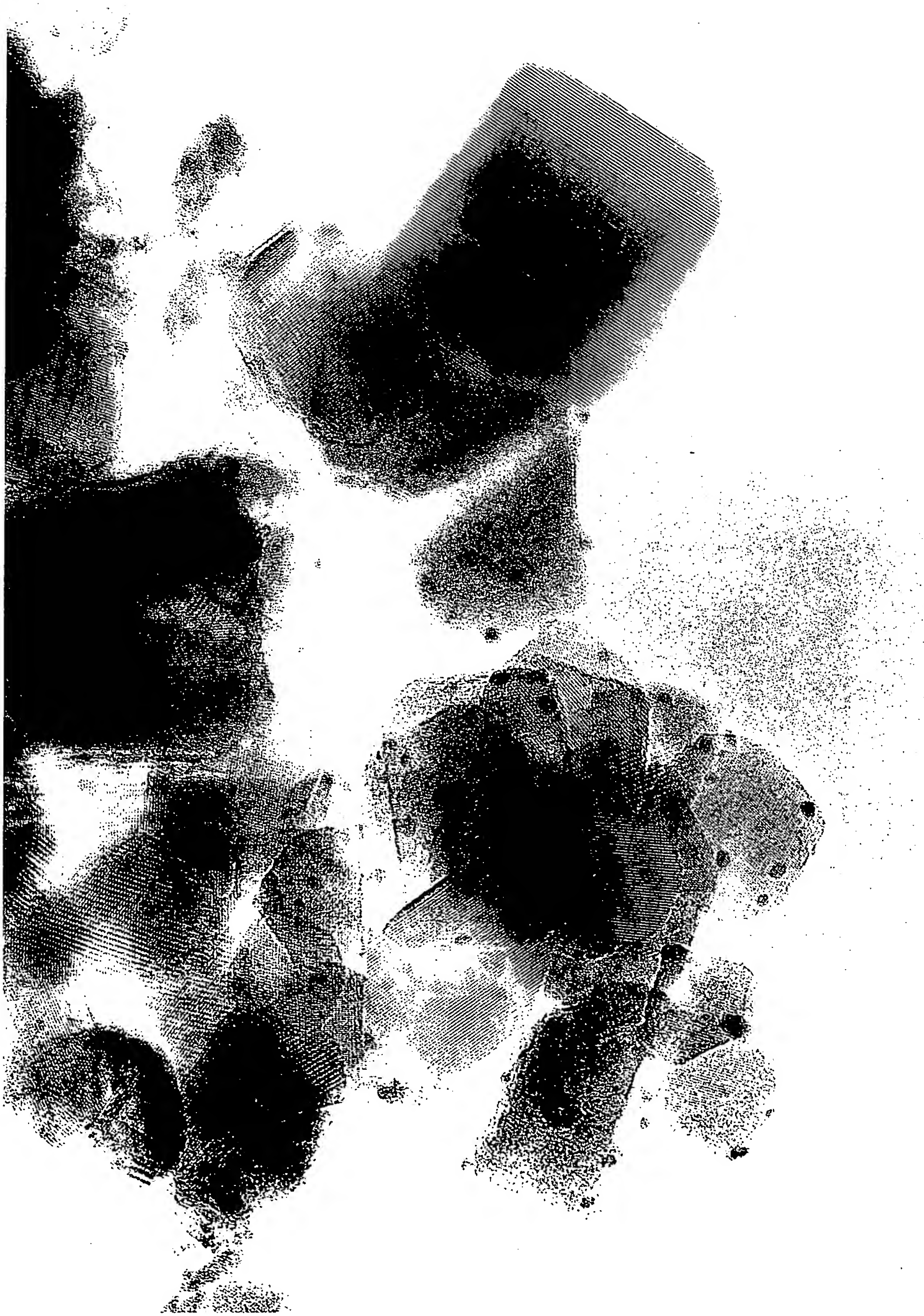

Photo. 3